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## Microstructure-Property Relationship in Nanocomposite Fibers Prepared by Continuous Melt Compounding

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Further development of the concept of hybrid organic/inorganic nanocomposites resulted in the continuous preparation of nanocomposite fibers *via* melt compounding where the polymeric fiber matrix is reinforced by organically modified montmorillonite. Samples containing different amounts of nanoclay prepared by melt intercalation process in a twin screw extruder and then melt spun into the fibers. The nanocomposite samples characterized using X-ray diffraction patterns, differential scanning calorimetry, scanning electron microscopy and melt viscoelastic results along with mechanical analyses. The nanocomposite samples showed different microstructural behaviour in nanoscale due to the presence of different amounts of organoclay incorporated in the polymeric matrix. The results also demonstrated that addition of 3 wt. % organoclay was optimal to improve microstructure and properties of poly(butylene terephthalate) nanocomposite fibers prepared by continuous melt compounding.

**Keywords:** Nanocomposite fiber, Melt compounding, Melt viscoelastic, Microstructure.

### INTRODUCTION

Polymeric nanocomposites, which can be produced by using different nanoparticles (*e.g.* carbon nanotube, carbon nanofiber, nanoclay, nanosphere), have received considerable attention because of their improved properties. Polymer layered silicate nanocomposites have been studied due to the desirable characteristics for a variety of applications [1-7].

The final properties of the nanocomposites strongly affected by the nanoparticle characteristics (*e.g.* shape, size and aspect ratio), polymer matrix characteristics (*e.g.* polarity, molecular weight, viscosity and compatibility with the filler) and compatibilizer characteristics (*e.g.* polarity and molecular weight).

To produce nanocomposite with remarkable enhanced properties, it is necessary to develop microstructure by nanoparticle uniformly dispersion and distribution in the polymeric matrix. Therefore, various factors affecting the final microstructure of the polymer nanocomposite should be considered [8-14]. Among different methods for producing the layered silicate nanocomposites, melt intercalation process due to its versatility, low cost and compatibility with polymer manufacturing process is industrially valuable technique [15,16].

It is worth highlighting that in the melt intercalation process, the nanocomposites can be formulate and produced

directly by conventional melt compounding process. This method comprises using the ordinary compounding and forming devises for developing polymeric materials with enhanced properties. Melt rheological behaviour of the polymeric materials plays an important role to affect the extent of nanoclay exfoliation due to apply the hydrodynamic separation forces by the matrix [17-20]. The exfoliation type morphology is the preferred structure to improve final properties of the nanocomposites, where the nanoclay platelets can distribute homogenously in all over the polymer matrix and form a three dimensional physical structure at higher nanoclay loadings [21-22].

One of the commercially available semi-crystalline polyesters and thermoplastic engineering polymeric materials with good processability and properties is poly(butylene terephthalate) (PBT) [23-27]. Li *et al.* [28] studied the microstructure and mechanical properties of PBT/nanoclay nanocomposites prepared by melt compounding. They focused on the effect of the nanoclay dispersion on final properties of resulting nanocomposites. Wu *et al.* [29] indicated the influence of nanoclay concentration on crystallization and rheological behaviour of PBT/nanoclay hybrids. Chang [30] compared the morphologies and thermo-mechanical properties of polyester nanocomposite fibers with different nanoclay content and drawing ratio which prepared by *in situ* preparation.

Although a few research works have been devoted to the parameters affecting microstructure development of the PBT nanocomposites, the research reported on the role of nanoclay on the properties enhancement of PBT fibers prepared by continuous melt compounding is rare. In this research, the influences of microstructure and morphology on mechanical properties at various nanoclay loadings of PBT/nanoclay nanocomposite fibers prepared by continuous melt compounding were investigated.

## EXPERIMENTAL

Poly(butylene terephthalate), type Pocan® B 1505 supplied by Bayer Chemical Co. (Germany), was used as polymeric matrix. The Cloisite 30B (commercially abbreviated C30B), used as organoclay, purchased from Southern Clay Products (USA).

**Sample preparation:** The poly(butylene terephthalate) nanocomposites containing different amounts of nanoclay (1, 3 and 5 wt. %) were considered. Prior to the melt processing, PBT and the organoclay were dried at 80 °C under reduced pressure for a day. The melt compounding process was conducted in a co-rotating twin extruder by using matrix based masterbatch feeding method. First the PBT and nanoclay with the ratio PBT/nanoclay: 2/1 melt blended and then an appropriate amount of the PBT and masterbatch were melt compounded. The resulting nanocomposites continuously were melt-spun as illustrated in Fig. 1. The twin extruder temperature zones controlled at 220, 240, 245, 245 and 240 °C. The spinneret of the melt spinning machine (Brabender) contained 20 orifices (each 1 mm in diameter). To improve the physical and mechanical properties hot drawing of the fiber samples was carried out.

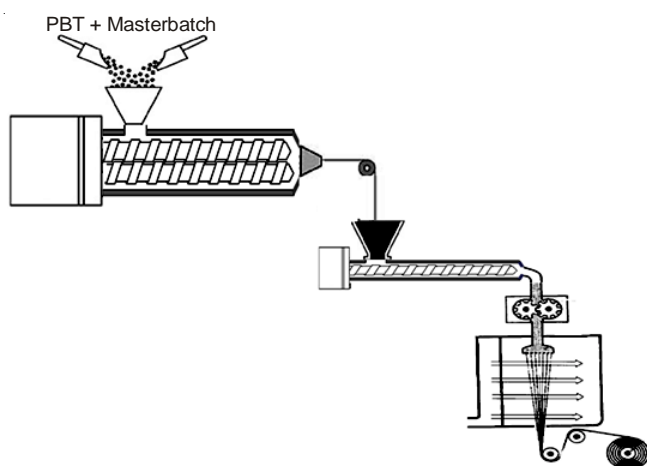


Fig. 1. Schematic diagram of continuous nanocomposite fibers production by using PBT based masterbatch feeding method

**Characterization:** The wide angle X-ray diffraction (WAXD) was performed on the nanoclay and nanocomposite samples to evaluate the extent of interlayer spacing enlargement by using a Phillips X-ray diffractometer operated at 40 kV and 40 mA (Cu-K $\alpha$  radiation, wavelength ( $\lambda$ ) 0.154 nm). The dynamic rheological measurements of the samples were performed in the Paar physica USD 200 (Austria) using 25 mm parallel plates in oscillatory mode. The tests were conducted at the strain sweep, frequency range of 0.1-1000 s<sup>-1</sup> at 250 °C

and 1 % strain amplitude. The nanocomposite samples were fractured under liquid nitrogen and coated with gold to avoid any charge generated by the electron beam. The morphology of the samples was then analyzed by using scanning electron microscopy (Phillips XL30, Netherlands). Differential scanning calorimetry (DSC) spectra of the samples were recorded on a Perkin-Elmer calorimeter (USA). The samples were heated at rate 5 °C/min to the temperature of 300 °C and kept for 3 min in order to eliminate all thermal history and then were cooled to 25 °C to study the crystallization behaviour. The tensile measurements of the fibers determined by Shirley Micro 50 tester. The gauge length of 25 mm and crosshead speed of 50 mm/min were used at room temperature.

## RESULTS AND DISCUSSION

Fig. 2 shows XRD patterns of the PBT/nanoclay nanocomposite samples with different nanoclay concentration. The organoclay (Cloisite 30B) shows the  $d_{001}$  peak corresponding to the 18.5 Å interlayer spacing at  $2\theta = 4.73$ . As it was expected a highly intercalated morphology obtained from PBT/nanoclay samples especially at low organoclay content. The results demonstrated the acceptable extent of melt intercalation for continuous melt compounding by using matrix based masterbatch feeding method.

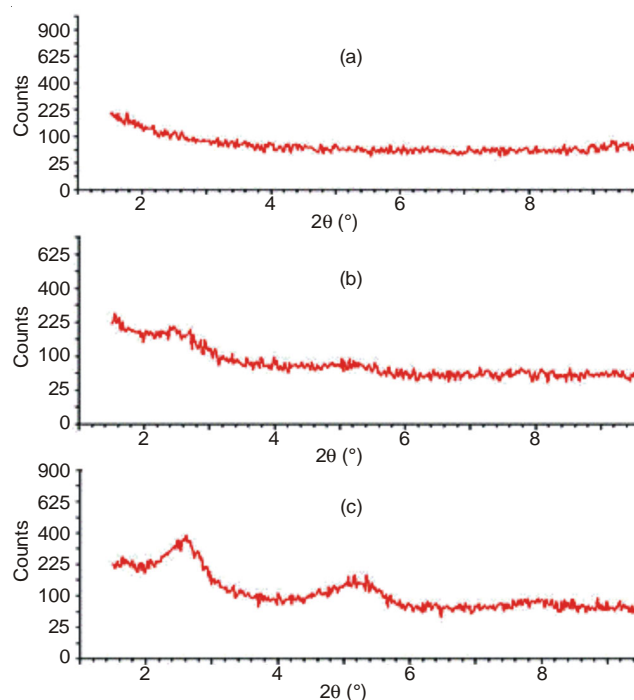


Fig. 2. XRD patterns of neat organoclay (Cloisite 30B) and PBT nanocomposite fibers with different nanoclay content: (a) 1 wt. %, (b) 3 wt. %, (c) 5 wt. %

By comparing these results, one may conclude that at low organoclay loadings, nanoclay dispersed without any aggregation and agglomeration in the PBT matrix. On the other hand, at higher nanoclay loadings, the specific peaks of nanoclay appeared and became stronger by increasing the content of nanoclay in the PBT phase. The nanocomposite sample containing 5 wt. % organoclay shows two peaks suggesting that two populations of non-exfoliated clay co-existed (Fig. 2c).

Fig. 3 presents the melt linear viscoelastic properties for PBT and its nanocomposites. It can be seen that the PBT nanocomposite sample containing 3wt. % nanoclay exhibited a pronounced low frequently non-terminal behaviour in storage modulus and strong viscosity upturn. These results revealed formation of the three dimensional physical network between nanoclay platelets and polymer chains. This is a good evidence for exfoliated type morphology.

The nanocomposite sample containing 1 wt. % nanoclay exhibits behaviour similar to the neat PBT, signifying that the amount of nanoclay in the PBT matrix phase was not enough to form a network.

The evolution of the nanoclay dispersion in the polymeric matrix as a function of nanoclay content was confirmed by

SEM analysis. Fig. 4 presents the SEM micrographs of the resulting nanocomposite fibers with different nanoclay concentration. While PBT and organoclay were marginally compatible, the extent of organoclay loading plays an important role in morphology development. Three dimensional network formed between PBT polymeric chains and nanoclay (Fig. 4b and 4d) can improve the nanocomposite properties due to better transferring stress between phases to increase intrinsic strength.

The characteristics of components as well as the fraction of nanofiller determine the final morphology of the nanocomposite fibers. The number of tactoids and agglomerates observed in Fig. 5, indicated the aggregation of nanoclay in this sample. At high organoclay loading (5wt. % organoclay), the system was saturated and thermodynamic could not force

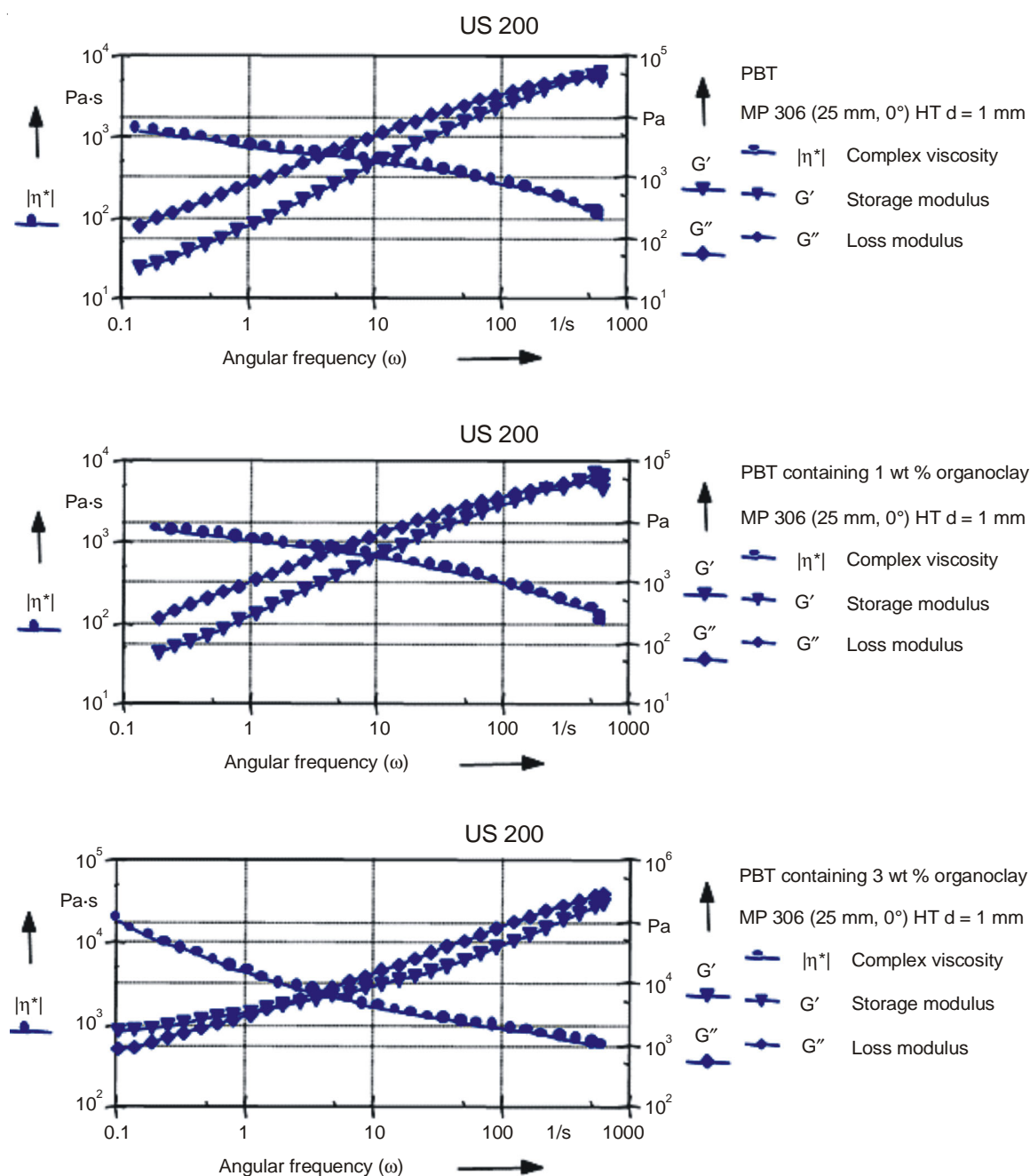


Fig. 3. Melt linear viscoelastic properties of neat PBT and PBT nanocomposites with 1 wt. % and 3 wt. % organoclay



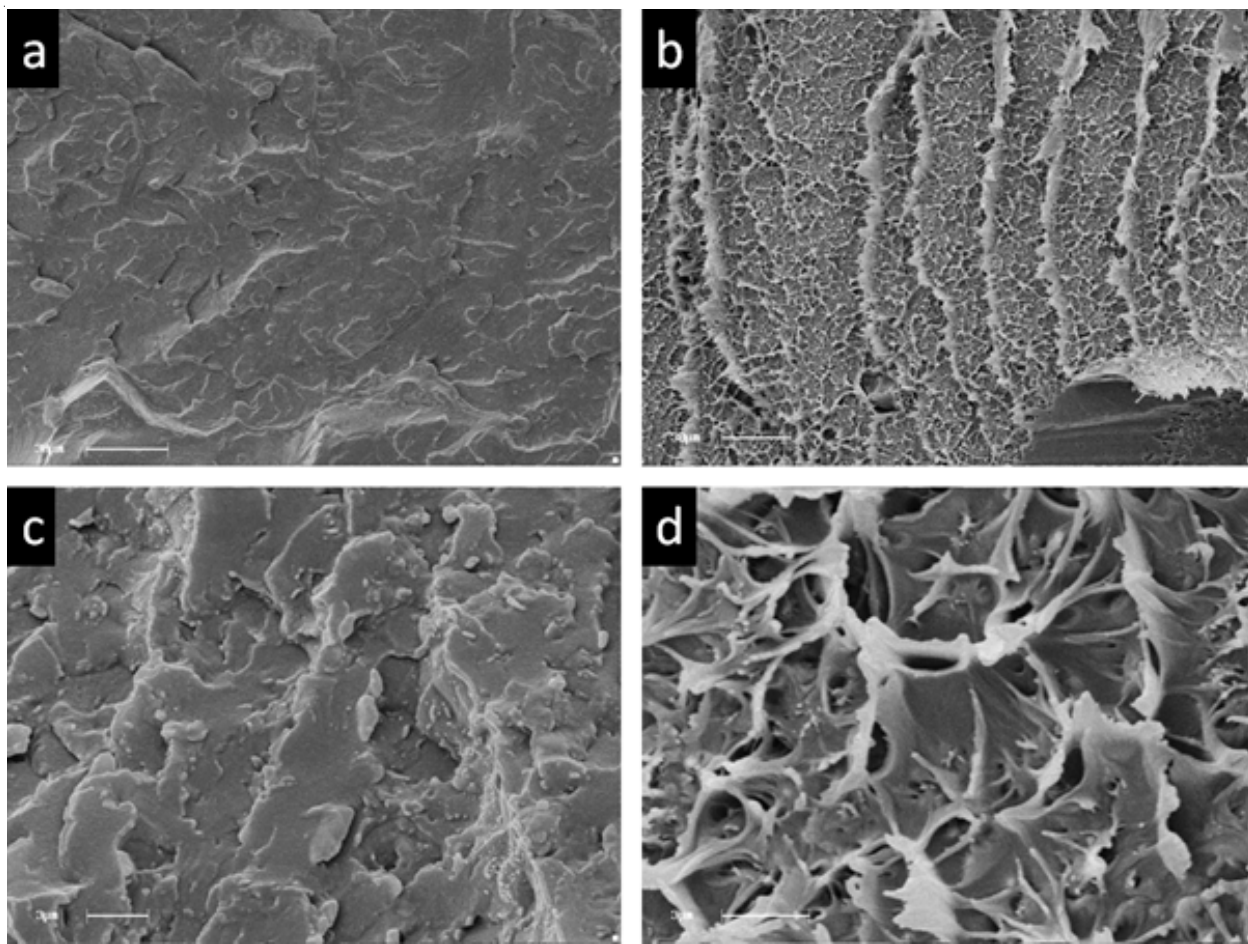


Fig. 4. SEM micrographs of fiber samples with different nanoclay concentration at different magnifications: (a,c) 1 wt. % organoclay, (b,d) 3 wt. % organoclay

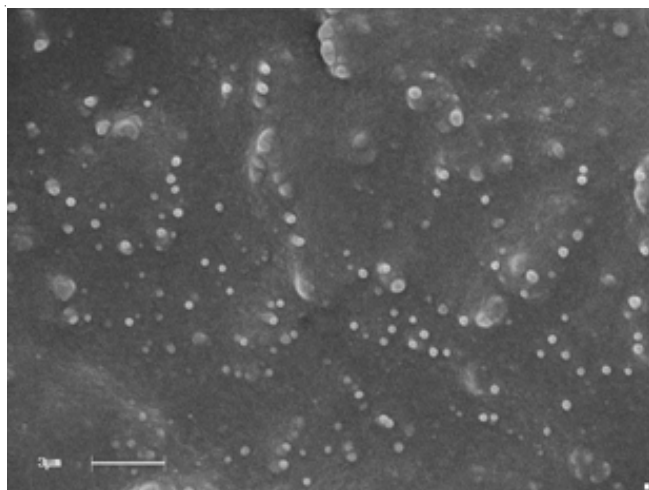


Fig. 5. SEM micrographs of nanoclay aggregation in PBT nanocomposite fiber containing 5 wt. % organoclay

polymeric chains to enter the gallery between nanoclay platelets. The morphology of the hybrid fibers depends on the concentration of nanoclay in the system, the interaction between the polymeric chains and the nanolayers and also the thermodynamic parameters in the melt state.

The thermal behaviour of PBT/nanoclay nanocomposite fibers with different amounts of nanoclay is presented in Fig. 6. From these results one may notice that the crystallinity of PBT

shows a positive deviation from mixture law in the presence of nanoclay. At lower nanoclay content, the exfoliated nanoclay platelets increased the crystalline phase by nucleating effect. On the other hand, at higher nanoclay loadings part of silicate layers hindered the chain motion and transferring to the crystal cell.

An important aspect of studying the crystallization behaviour of the nanocomposites with higher nanoclay loading is to investigate the effect of nanolayer as nucleating agent and also nanofiller on the extent and the shape of nanometric polymeric crystal cell. Furthermore, the three dimensional physical nanostructure formed between nanolayers and polymeric chains has considerable effects on the crystallization behaviour and final microstructure of nanocomposite fibers. However, the dispersion and distribution of the nanoclay platelets and/or tactoids in the matrix have important effects on the crystallization behaviour of the polymeric phase, where the arrangement of the nanoscopic crystal cell can be influenced by morphology of the inorganic nanolayer in the polymeric matrix. The DSC measurements also demonstrated that the presence of nanoplatelet affected the  $T_g$  with hindering conformation in the amorphous region.

The results of tensile test performed on the PBT fiber samples presented in Fig. 7. As it can be noticed from these results, strength and modulus of the PBT nanocomposite fibers increased by incorporation of organoclay. It is also observed

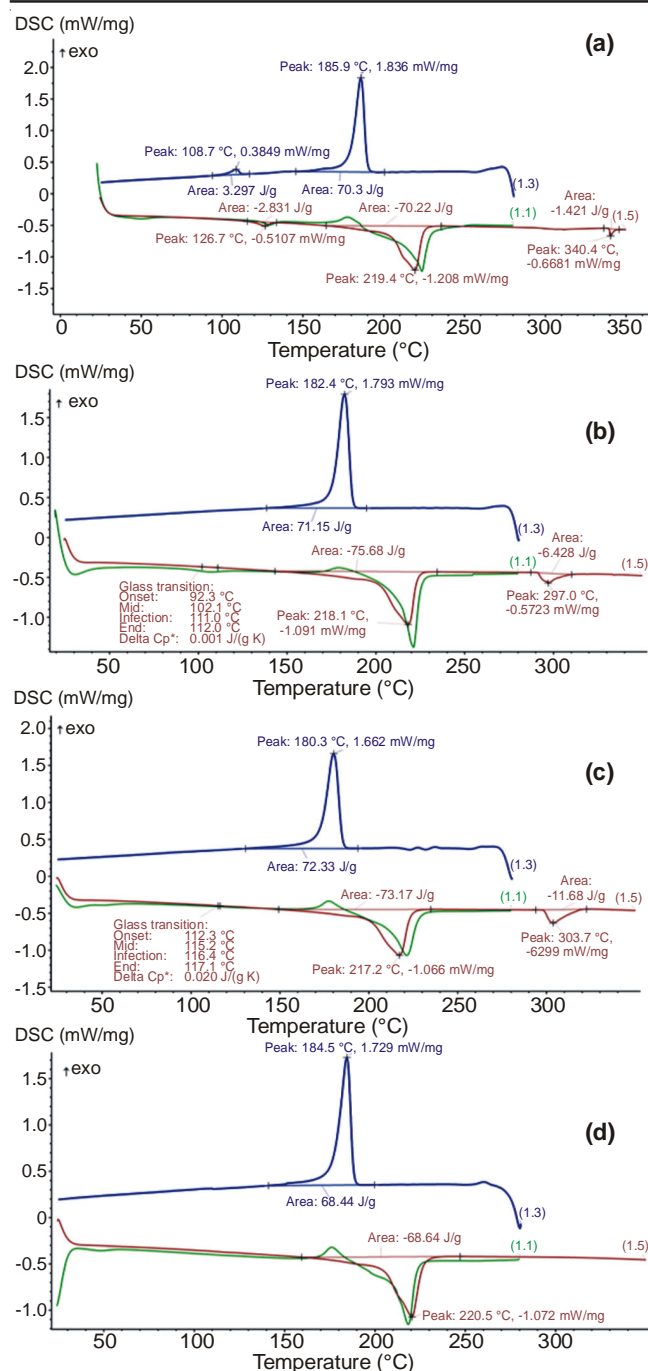


Fig. 6. DSC heating and cooling thermograms of PBT and PBT nanocomposite fibers containing different amounts of organoclay: (a) neat PBT; (b) 1 wt. %; (c) 3 wt. %; (d) 5 wt. %

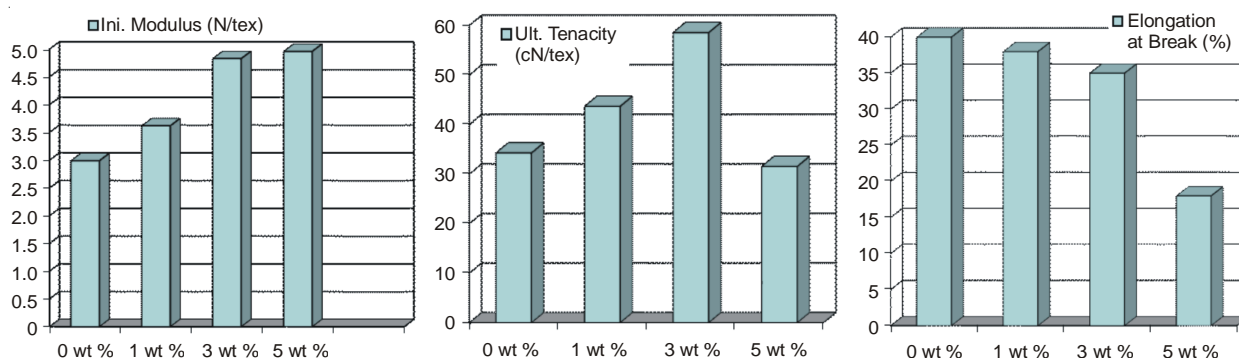


Fig. 7. Mechanical properties of PBT nanocomposite fibers containing different amounts of organoclay

that increase in the strength as well as modulus did not increase linearly with increasing the organoclay concentration. The nanocomposite fibers containing more than 1 wt. % organoclay showed superior mechanical properties compared to the conventional PBT fiber. This can be explained as result of the three dimensional network formation by exfoliated nanoclay platelets as reinforcing agent in the matrix *via* melt compounding. This is also evidenced by XRD, RMS and SEM. Therefore, the presence of nanoclay layers as mineral structure in addition to the nanostructure formed between the nanolayers and polymeric chains improved the mechanical properties. As mentioned above the influence of the crystalline structure on the final mechanical properties should also be considered. Incorporation of nanoclay with exfoliated morphology can improve the mechanical properties by transferring stress between nanoclay network and polymer chains. It suggests that the mechanical performance of nanocomposite fibers depends on two factors: the adhesion quality between PBT matrix and nanoclay platelets and the aspect ratios (length/thickness ratio) of the reinforcing elements. It should be noted that appropriate processing design and feeding system led to considerable improvement in physical and mechanical properties of the nanocomposite fibers by increasing the extent of the melt intercalation even in the continuous preparation process.

### Conclusion

The aim of this research was to study the PBT fiber microstructure and properties enhancement by incorporation of different amounts of organoclay *via* continuous melt compounding. Based on the WAXD and melt viscoelastic results, it was found that the PBT matrix intercalated the nanoclay during continuous melt compounding due to affinity of organoclay with polar PBT matrix. Morphological observations demonstrated that the nanoclay platelets and/or tactoids influenced the morphology of nanocomposite fibers in each organoclay loading. The DSC results indicated that addition of organoclay influenced thermal behaviour of the PBT fibers depending on the extent of organoclay loading and intercalation. The results of this research suggest that microstructure-properties relationships affected by number of morphological factors such as heterogeneity of nanoscale arrangement, organic-inorganic interaction and the nanoclay layers arrangement. Since only small amount of the organoclay needed to achieve desired characteristics of the fibers during continuous melt compounding, there is potential for this new class of polymeric nanocomposite materials in the fiber industry.

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